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U.S. PATENT APPLICATION

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Title: NANOPOROUS AND MICROPOROUS MANUFACTS BASED ON
SYNDIOTACTIC POLYSTYRENE AND PROCESSES FOR THEIR
PREPARATION

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SPECIFICATION

NANOPOROUS AND MICROPOROUS MANUFACTS BASED ON
SYNDIOTACTIC POLYSTYRENE AND PROCESSES FOR THEIR
PREPARATION

DESCRIPTION

5 The present invention relates to microporous
manufacts (i.e, manufact presenting high porosity, often
referred as aerogels) based on syndiotactic polystyrene
and characterized by the presence of cavities with
nanometric dimensions characteristic of the δ crystalline
10 form and to processes for their preparation. These
manufacts are capable to absorb with a fast kinetics
volatile organic compounds from liquid or gaseous phases,
also when such components are present at very low
concentrations.

15 Background of the invention

The present invention is located in the technical-
scientific fields of industrial chemistry and
engineering, and more specifically in the area of the
molecular analysis and separation and it provides
20 possible industrial uses for environment pollution
control.

It is well-known that syndiotactic polystyrene (s-
PS) is a thermoplastic semi-crystalline polymer which
presents a complex polymorphism. In particular, two
25 crystalline forms (α and β) characterized by a trans-
planar zig-zag chain conformation can be obtained by
starting from the melt processes while two other
crystalline forms (γ and δ) characterized by a $s(2/1)2$
helical chain conformation are obtained from solution
30 processes. Furthermore, it is also known that the δ form
is a nanoporous crystalline form, which can be obtained
by removal of low molecular weight guest molecules from
clathrate crystalline forms. Such δ -form is characterized
by X-ray diffraction patterns presenting high intensity
35 reflections at 2θ ($\text{CuK}\alpha$) \approx 8.4° , 10.6° , 13.6° , 17.2° ,
 20.8° , 23.6° , and by an intensity ratio between two
reflections presenting Miller indexes (010) and ($\bar{2}10$),

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that is $I(8.4^\circ)/I(10.6^\circ)$, larger than 5. Samples containing δ -phase are able to absorb readily, in the crystalline phase, volatile organic compounds from liquid or gaseous mixtures (i.e. to form clathrate), also when
5 those components are present at low concentrations.

Italian patent IT1228915 teaches that manufactures in δ form can be preferably obtained from semi-crystalline clathrate manufactures in δ -form by guest removal with solvents, or with gas flow; suitable solvents are acetone
10 and methyl-ethyl-ketone.

In Italian patent application No. SA98A000008 a process to obtain and regenerate nanoporous semicrystalline polymeric materials is described based on syndiotactic polystyrene, which is based on an extraction
15 procedure with liquid or supercritical carbon dioxide. According to the teaching of this patent, this process and the other processes described in the Italian patent IT1228915 are efficient when they are applied to semicrystalline clathrate samples, for which the solvent
20 content is lower than 100 wt% of the dry polymer, i.e. when the polymer concentration is larger than 50 wt%.

It is also well-known that the diffusion kinetics (sorption and desorption) of volatile organic compounds are strongly dependent on the morphology of the
25 semicrystalline manufactures. In particular, fine powders present fast sorption kinetics but are difficult to handle. On the other hand, morphologies with low specific surface (film, sheet) are easier to handle in molecular separation processes but they display much slower
30 diffusion kinetics. For example, as described in Italian patent application no. SA2000A000023, polymer films can be used as sensing elements for the detection of chemical substances (for example in resonant sensors) since they show the advantage of being rigid and at the same time
35 they present a higher sensitivity and selectivity than other polymeric sensing films used so far. However, such films have the drawback of slower sorption kinetics and

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thus the sensor response time is larger with respect to technologies based on the absorption of the pollutant in amorphous phases.

5 There was therefore a need in the art to provide polymeric materials characterized by fast sorption kinetics while maintaining a good handiness, which could also be efficiently used for molecular separations and for molecular sensors.

10 It has now been surprisingly found that specific manufacts based on syndiotactic polystyrene homopolymers or copolymers, presenting the nanoporous δ phase can solve this problem.

15 Objects of the present invention are therefore microporous and nanoporous manufacts based on syndiotactic polystyrene in the δ crystalline form with an apparent density between 0.001-0.8 g/cm³ and a percentage of crystalline form between 5-70% obtainable according the process comprising the following steps:

20 a) preparation of a gel based on homopolymers or copolymers of syndiotactic styrene, with a polymer concentration between 0.1 and 50 wt% in a solvent or a mixture of solvents, at least one of said solvents being a suitable guest of a crystalline clathrate phase, of syndiotactic polystyrene, wherein the copolymers can
25 contain as comonomers CH₂=CH-R olefins, wherein R is an alkyl-aryl or a substituted aryl radical with 6-20 carbon atoms.

30 b) Removal of the solvent from the gel by liquid or supercritical carbon dioxide extraction process, operating at pressures between 50 and 350 bar and temperature between 20 and 70°C.

BRIEF DESCRIPTION OF DRAWINGS

The present description contains seven drawings showing:

35 Fig. 1 a scanning electron micrograph of a section of manufact prepared according to Example 1 showing a fibrillar morphology

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Fig. 2 the X-ray diffraction pattern ($\text{CuK}\alpha$) of a manufact prepared according to Example 1.

Fig 3 a comparison between the sorption kinetics of: the microporous manufact prepared according to Example 1 and a film of 8 μm thickness (both in nanoporous δ -phase), and a microporous manufact according to the Comparative Example 1 (in β phase).

Fig. 4 the chloroform sorption kinetics obtained at a temperature $T = 35^\circ\text{C}$ and a pressure $P = 2$ Torr for a manufact according to Example 1.

Fig.5 a scanning electron micrograph of a section of manufact prepared according to Comparative Example 1, showing a lamellar morphology.

Fig. 6 the X-ray diffraction pattern ($\text{CuK}\alpha$) of the manufact prepared according to Comparative Example 1.

Fig. 7. a scanning electron micrograph of a section of the manufact according to Example 2.

The manufactures object of the present invention are microporous as their apparent density is $0.8 - 0.001 \text{ g/cm}^3$, preferably $0.3 - 0.003 \text{ g/cm}^3$. In addition, these manufactures are semi-crystalline and include a percentage of crystalline δ phase between 5 and 70%, preferably larger than 10% and, thus, are also nanoporous since it is known that the δ -phase of syndiotactic polystyrene is nanoporous. The principal advantage of these new manufactures is to present sorption kinetics of volatile organic compounds much faster than those of films and similar to those of fine powders, maintaining at the same time a good handiness.

Within the present description, under manufact is meant the polymeric material based on syndiotactic polystyrene obtained according to the invention.

For syndiotactic polystyrene (sPS), a polymer with syndiotactic sequences of the polymer chain long enough to allow the polymer crystallization into the nanoporous crystalline form is meant. This polymer can be for example synthesized following the procedure described in

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the European patent N°0271875-Himont Italia. In addition to syndiotactic polystyrene homopolymers, styrene copolymers with $\text{CH}_2=\text{CH-R}$ olefins, where R is an alkyl-aryl or a substituted-aryl radical with 6-20 carbon atoms with microstructure prevailingly syndiotactic and crystallizable in the nanoporous crystalline δ form, are also included in the definition of manufacts based on syndiotactic polystyrene.

The SPS nanoporous crystalline form according to Italian patent no. 127842 is characterized by a X-ray diffraction pattern presenting high intensity reflections at 2θ ($\text{CuK}\alpha$) $\approx 8.4^\circ$, 10.6° , 13.6° , 17.2° , 20.8° , 23.6° , and by an intensity ratio between two reflections presenting Miller indexes (010) and ($\bar{2}10$), that is $I(8.4^\circ)/I(10.6^\circ)$, larger than 5. For unoriented samples, the crystallinity index can be easily determined from the X-ray diffraction patterns using the classical method of Hermans and Weidinger. According to this method the crystallinity index is given by the ratio of the diffraction area due to the crystalline phase and the total diffraction area.

Volatile organic compounds which can be sorbed are all the compounds that, after sorption in the nanoporous crystalline δ form, can lead to the formation of crystalline clathrate forms, these compounds thus becoming guest molecules of the clathrate structure. Among these compounds can be cited halogenated molecules (like e.g., chloroform, methylene chloride, carbon tetrachloride, dichloroethane, trichloroethylene, tetrachloroethylene, dibromoethane, methyleneiodide, etc.), aromatic molecules (like e.g. benzene, toluene, styrene, etc.), cyclic molecules (like e.g. cyclohexane, tetrahydrofuran, etc.). It is worth noting that the manufacts are sensitive to the volatile organic compounds most frequently present in industrial wastes, like benzene, toluene, chloroform, methylene chloride, tetrachloroethylene, trichloroethylene, chlorobenzenes,

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styrene, and xylenes. The liquid and gaseous mixtures from which these compounds can be sorbed can be based on water or air.

5 The microporous and nanoporous manufacts are obtained in the present invention through processes comprising liquid or supercritical carbon dioxide extractions. These processes are applied to gels produced with a solvent which can be a guest of a crystalline clathrate phase of syndiotactic polystyrene said gels
10 containing a polymer based on syndiotactic polystyrene with polymer concentration between 50% and 0.1 wt%, preferably between 30% and 0.5 wt%.

Further object of the present invention is a process for obtaining microporous and nanoporous manufacts based
15 on syndiotactic polystyrene in δ form comprising the following steps:

a) preparation of a gel containing homopolymers or copolymers of syndiotactic polystyrene, at a polymer concentration between 0.1 and 50 wt% in a solvent or a
20 mixture of solvents, at least one of said solvents being a suitable guest of a clathrate phase of syndiotactic polystyrene, wherein the copolymers contain as monomers $\text{CH}_2=\text{CH}-\text{R}$ olefins, wherein R is an alkyl-aryl or a substituted-aryl radical with 6-20 carbon atoms.

25 b) removal of the solvent from the gel with liquid or supercritical carbon dioxide extraction at operating pressures between 50 and 350 bar and temperatures between 20 and 70°C.

Solvents which can be used, pure or in mixtures, for
30 the preparation of the gels described in the invention are benzene, toluene, styrene, decahydronaphthalene, tetrahydrofuran, 1,2-dichloroethane, chloroform, trichloroethylene, carbon disulfide.

The above-mentioned gels can be both of physical
35 type, i.e. characterized by the absence of chemical cross-links between the polymer chains, or of chemical type but with a small amount of chemical cross-links.

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Physical gels can be obtained during the polymerization in liquid monomer or during the polymerization in solution of solvents, which in addition to solubilize the styrene, can also be suitable guests molecule of the δ -form of syndiotactic polystyrene.

Gels can be also obtained following the traditional procedures for obtaining physical gels which consist in the polymer dissolution in appropriate solvents, followed by a rapid cooling of the solution.

Chemical gels, i.e. gels containing cross-linked polymers, based on syndiotactic polystyrene, can be easily obtained during the polymerization using vinyl comonomers with at least two functional groups such as, for example, p-divinylbenzene, o-divinylbenzene, etc. In order to ensure that the cross-linked polymer can crystallize it is necessary that only a small amount of cross-links is present and this can be achieved using a low molar ratio between the at least bi-functional monomers and the styrene. In particular, the fraction of comonomer units derived from at least bi-functional monomers has to be between 20 and 0.1 mol%, more preferably below 10 mol%.

The essential characterizing feature of the process according to the present invention is that the removal of the solvent from the gel not only leads to manufactures whose crystalline phase is the nanoporous δ phase but also occurs without any modification of the macroscopic dimensions of the initial gels. This feature is even more surprising if we consider that the process can be applied not only to chemical gels with a low degree of cross-linking but also to physical gels. In the light of the small amount or the total absence of chemical cross-links the collapse of the gel during the removal of the solvent constituting the principal component of the gel was to be expected. As a matter of fact, it is known in the art that if the solvent evaporates, its surface tension acts on the internal structure of the gel and produces its

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collapse. This does not happen in the process of the invention.

5 In the case of chemical gels with high degrees of cross-linking such as, for example, those obtained from thermosetting materials like resorcinol-formaldehyde and melamine-formaldehyde, traditional solvent removal processes require to bring the solvent to its supercritical conditions or to exchange the solvent with a more volatile solvent which needs to reach, in turn, 10 supercritical conditions. These extraction procedures ensure the elimination of liquid-vapor surface tension and thereby the accompanying capillary pressure, which acts to collapse the gel network, and thus allow to maintain the three-dimensional gel structure. Presently, 15 the preferred technique to remove solvents from highly crosslinked chemical gels uses carbon dioxide as supercritical drying agent, which allows the drying step to be done under milder conditions and improved safety.

20 In the present invention the process of supercritical drying by carbon dioxide is applied to physical gels or weakly crosslinked chemical gels based on syndiotactic polystyrene and, surprisingly, this procedure leaves essentially unaltered the initial macroscopic size of the gel, although the fraction of the 25 removed solvent can be as high as 99%.

In the present invention under weakly cross-linked chemical gels are meant gels wherein the fraction of comonomeric units derived from at least bifunctional monomers (the cross-linking units) is comprised between 0.1 and 20 mol %, preferably lower than 10 mol %. 30

The manufactures according to the invention are obtained through processes comprising an extraction with liquid or supercritical carbon dioxide at operating pressures between 50 and 350 bar and operating 35 temperatures between 20 and 70 °C, more preferably between 25 and 60°C.

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In a particularly preferred embodiment, said gels are obtained directly during the syndiospecific polymerization of styrene monomers (or possibly with the above mentioned comonomers) using, for example, the method described in the European patent N°0271875 where the polymerization catalysis takes place in liquid monomer. Therefore, is further object of the present invention a process in which the preparation of the gel, based on syndiotactic homopolymer or copolymers of styrene, takes place in situ through syndiospecific polymerization of styrene which acts both as monomer and solvent of the reaction.

A further object of the present invention are devices and, or sensors for the detection of volatile organic compounds containing the manufactures of the present invention.

The following examples are supplied in order to illustrate the invention without limiting the scope thereof.

Example 1:

The syndiotactic polystyrene homopolymer was supplied by "DOW Chemical" under the trademark Questra 101. The polymer was dissolved in chloroform (10 wt% solution) at 110°C in a hermetic test tube. Then, the solution was quenched at room temperature and a physical gel with a cylindrical shape and dimensions 5 mm x 25 mm is obtained in the test tube.

The gel was treated with a supercritical carbon dioxide extraction procedure ($T = 45^{\circ}\text{C}$, $P = 200$ bar, extraction time $t = 300$ min). After extraction, the manufacture maintains the form and dimensions of the native gel and presents an amount of solvent molecules below 1 wt%. The apparent density of the manufacture is 0.18 g/cm^3 and, as shown in the scanning electron micrograph reported in Fig.1, a fibrillar morphology with fiber diameter between 50 and 100 nm is obtained. The X-ray diffraction pattern ($\text{CuK}\alpha$) of this manufacture, reported in

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Figure 2, displays strong reflections located at c.a. 8.4°, 10.6°, 13.3°, 16.8°, 20.7°, 23.5° with a ratio of the two reflections $I(8.4^\circ)/I(10.6^\circ)$ larger than 15. This indicates that the manufact obtained after the solvent extraction procedure is characterized by the nanoporous crystalline δ phase. The manufact crystallinity, determined from the ratio of the diffraction area due to the crystalline phase and the total diffraction area, is equal to 40%.

The manufact exhibits high sorption kinetics of volatile organic compounds. As an example, the chloroform sorption kinetics obtained at $P = 5$ torr and $T = 56^\circ\text{C}$ for this manufact and for a semicrystalline δ -form syndiotactic polystyrene film, having a thickness of 8 μm and prepared according to the teaching of Italian patent application no. SA00A00023, are compared in Figure 3. It comes out from Figure 3 that the chloroform sorption velocity at $P = 5$ torr and $T = 56^\circ\text{C}$ rises by a factor 15 when using the new microcoporous and nanoporous manufact instead of the nanoporous film.

The chloroform sorption kinetics obtained at $P = 2$ torr and $T = 35^\circ\text{C}$ with the manufact is also shown in Figure 4.

Comparative Example 1:

Syndiotactic polystyrene homopolymer of Example 1 was dissolved into chlorotetradecane (10 wt% solution) at $T = 220^\circ\text{C}$ in an hermetic test tube. Then the solution was quenched at room temperature and a physical gel with a cylindrical shape and dimensions 5mm x 25mm was obtained in the test tube.

The gel was treated with a supercritical carbon dioxide extraction procedure ($T = 45^\circ\text{C}$, $P = 180$ bar, extraction time $t = 280$ min). Similarly to example 1, after the extraction procedure, the manufact maintains the form and dimensions of the native gel with an amount of solvent molecules below 1 wt%.

The apparent density of the manufact obtained is

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0.10 g/cm³ and as shown in the scanning electron micrograph reported in Fig. 5, a lamellar morphology is obtained.

5 The x-ray diffraction pattern (CuK α) reported in Fig. 6 displays strong reflections located at c.a. 6.1°, 10.4°, 12.25°, 13.55°, 18.50°, 20.20°. This indicates that the manufact obtained after solvent extraction procedure is characterized by the β crystalline phase. The crystallinity, determined from the ratio of the
10 diffraction area due to the crystalline phase and the total diffraction area, is equal to 48%.

Despite a lower apparent density than the manufact of Example 1, the manufact of this comparative example displays a much lower sorption capacity of volatile
15 organic compounds. For example, the chloroform sorption kinetics obtained at a pressure $P = 5$ torr and a temperature $T = 56^\circ\text{C}$ is compared in Figure 3 with the sorption kinetics of the manufact obtained in Example 1.

Example 2:

20 Syndiotactic polystyrene homopolymer of Example 1 was dissolved into 1,2-dichloroethane (2 wt% solution) at 170°C in a hermetic test tube. Then, the solution was quenched at room temperature and a physical gel with a cylindrical shape and dimensions 5mm x 25mm was obtained
25 in the test tube. The gel obtained shows a viscoelastic behavior with shear moduli measured at 1 rad/s $G' = 6.9 \times 10^3$ Pa and $G'' = 8.6 \times 10^2$ Pa.

The gel was treated with a supercritical carbon dioxide extraction procedure ($T = 40^\circ\text{C}$, $P = 230$ bar, extraction time $t = 220$ min). After the extraction
30 procedure, the manufact maintains the form and dimensions of the native gel with an amount of solvent molecules below 1 wt%.

The apparent density of the manufact obtained is
35 0.043 g/cm³ and, as shown in the scanning electron micrograph reported in Fig. 7, a fibrillar morphology with fiber diameter between 50 and 100 nm is obtained.

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Furthermore, as shown from the X-ray diffraction pattern ($\text{CuK}\alpha$), the manufact obtained after solvent extraction procedure is characterized by the nanoporous δ crystalline phase. The crystallinity, determined from the ratio of the diffraction area due to the crystalline phase and the total diffraction area, is equal to 44%.

Example 3:

Syndiotactic polystyrene homopolymer of Example 1 was dissolved into toluene (1 wt% solution) at 140°C in a hermetic test tube. Then, the solution was quenched at room temperature and a physical gel with a cylindrical shape and dimensions 5mm x 25mm was obtained in the test tube.

The gel was treated with a supercritical carbon dioxide extraction procedure ($T = 40^\circ\text{C}$, $P = 200$ bar, extraction time $t = 60$ min). After the extraction procedure, the manufact maintains the form and dimensions of the native gel with an amount of solvent molecules below 1 wt%.

The manufact obtained has an apparent density 0.014 g/cm^3 and is characterized by fibrillar morphology with fiber diameter between 40 and 70 nm. Furthermore, the manufact obtained after the extraction process includes the nanoporous crystalline form and has a crystallinity equal to 45%.

Example 4:

The syndiotactic polystyrene gel in styrene was achieved by polymerization at 50°C of 40 ml of styrene in a 100 mL flask under nitrogen atmosphere, by using 2 mg of cyclopentadienyl-titanium-trichloride (CpTiCl_3) and 290mg of methylalumoxane (MAO). The monomer was dried over calcium hydride for 48h under hydrogen atmosphere and distilled under a reduced pressure before use. The gel formation occurred already after 3 minutes of polymerization.

The gel was treated with a supercritical carbon dioxide extraction procedure ($T = 40^\circ\text{C}$, $P = 200$ bar,

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extraction time $t = 60$ min). After the extraction procedure, the manufacture maintains the form and dimensions of the native gel with an amount of solvent molecules below 1 wt%.

5 The manufacture obtained has an apparent density of. 0.18 g/cm^3 . Furthermore the manufacture obtained after the extraction procedure includes the nanoporous δ crystalline phase as shown by the X-ray diffraction pattern ($\text{CuK}\alpha$). The crystallinity, determined from the
10 ratio of the diffraction area due to the crystalline phase and the total diffraction area, is 30%.

Example 5:

This example relates to a procedure to remove the solvent present in the gel using carbon dioxide.

15 The procedure consists in the loading of the gel in a temperature-controlled vessel capable to operate in pressure conditions and then in the pressurization, at constant temperature, of the vessel with liquid or supercritical carbon dioxide up to the selected operating
20 pressure. The test involves a 60 min step without carbon dioxide flow, then a 70 to 150 min step under carbon dioxide flow in order to remove the mixture of solvent and supercritical fluid and finally 60 to 120 minutes of
25 a slow camera depressurization.